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Dipole moments of some molecules in solution

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The dipole moments of ten molecules in benzene solution have been calculated by using four different methods, *viz* Halverstadt & Kumler, Higasi, Scholte and Gilkerson & Srivastava. It has been found that Higasi method is very useful for all practical purposes

Introduction

Several methods have so far been proposed for the determination of dipole moment of a polar compound in a non-polar solvent. Both Higasi (1943, 1952) and Halverstadt & Kumler (1942) methods are based upon Debye's equation (1912) for dilute solutions. Halverstadt & Kumler method uses dielectric constant, density and refractive index data as a function of concentration, whereas Higasi method utilizes only dielectric and refractive index data. It has been shown by Krishna & Srivastava (1957, 1960) that the refractive index can also be dispensed away with. Scholte (1951) has developed a differential method based on Debye's equation corrected for the reaction field of the dipole (Onsager 1936). Gilkerson & Srivastava (1960, 1961) made a different approach and also suggested a method. It is, therefore, of interest to make a comparative study of these methods in order to justify one's utility over the other.

The dipole moments of seven substituted anilines, diphenyl ether, dibutyl ether and benzophenone have been calculated, by all the four methods listed above.

Experimental

The dielectric constant measurements were made at a frequency of 1 mc/sec. with the help of a Dielectrometer (Vij & Srivastava 1969). Density values were determined by using an Oswald Pycnometer having a bulb capacity of about 25 cc. Temperature of the experimental liquid was maintained with an accuracy of ± 0.03°C with the help of a Thermomix. Refractive indices were measured using an Abbey Refractometer reading to fourth decimal place. Accuracy in dielectric constant values was estimated to be $\pm 0.05\%$ and in density be $\pm 0.005\%$ Data were analyzed using the method of least squares and the determinod values of the dipole moments were estimated to be accurate within 1%

*The experimental observations in this papor were taken by J. K. Vij for his doctoral thesis.

Most of the values quoted in literature (McClellan 1963) of the dipole moments of compounds studied in this paper have been calculated using Halverstadt & Kumler's method (Bottcher 1952).

Results

A brief review of the different methods for determining the electric dipole is given below :

Higasi equation (1952) yields

$$\mu = B(a_0 - a_D)^{\frac{1}{2}} \qquad \ldots (1)$$

where a_0 and a_D are the slopes of dielectric constant and square of refractive index of the dilute solutions, respectively with weight fraction of the solute. B is a constant and is given by :

$$B = \frac{1}{2(\epsilon_1+2)}\left(\frac{27kTM_2}{\pi N_A d_1}\right)^{\frac{1}{2}}$$

All the parameters have their usual significances.

Halverstadt & Kumler equation (Bottcher 1952) states that

$$[P]_d^0 = \frac{\epsilon_1-1}{\epsilon_1+2}\cdot\frac{M_2}{d_1}\quad\frac{3M_1}{(\epsilon_1+2)^2 d_1}\left(\frac{\partial\epsilon}{\partial x_2}\right)_0 - \frac{M_1}{d_1^2}\,\frac{\epsilon_1-1}{\epsilon_1+2}\left(\frac{\partial d}{\partial x_2}\right)_0 \qquad (3)$$

where $(\partial\epsilon/\partial x_2)_0$ and $(\partial d/\partial x_2)_0$ are respectively, the slopes of the initial parts of the curves of dielectric constant and density versus mole fraction Other symbols stand for their usual significance From $[P]_d^0$ the value for orientation polarization $[P_0]_d^0$ is calculated by the relation

$$[P_0]_d^0 = [P]_d^0 - [P_e]_d^0 - [P_a]_d^0 \qquad (4)$$

Values of molar electronic polarization have been calculated by the procedure described by Bottcher (1952) and consequently the values of $[P_a]_d^0$ are estimated The dipole moment is then calculated by using the relation

$$[P_0]_d^0 = \frac{4\pi N_A \mu^2}{9kT} \qquad (5)$$

Scholte (1951), by his differential method for dilute solutions, obtained an equation :

$$\frac{\alpha_2}{1-f_2\alpha_2} + \frac{\mu^2}{3kT(1-f_2\alpha_2)^2} = \frac{(\epsilon_1-1)(2\epsilon_1+1)}{12\pi N_A c_1}\cdot\frac{M_1}{d_1}\left[\frac{M_2}{M_1} + \frac{(2\epsilon_1^2+1)}{c_1(\epsilon_1-1)(2\epsilon_1+1)}\left(\frac{\partial\epsilon}{\partial x_2}\right)_0 - \frac{1}{d_1}\left(\frac{\partial d}{\partial x_2}\right)_0 - \frac{\alpha_1}{1-f_1\alpha_1}\left(\frac{\partial f_1}{\partial x_2}\right)_0\right] Q_y. \qquad (6)$$

for spherical molecules.

In equation (6) α_2 is the average polarizability of the solute particle which can be calculated with the help of the equation :

$$\frac{n_2^2-1}{n_2^2+2} \cdot \frac{M_2}{d_2} = \frac{4\pi}{3} N_A \alpha_2 \qquad \ldots (7)$$

f_2 is the factor of the reaction field represented by the expression :

$$f_2 = \frac{1}{a_2^3} \frac{\epsilon_1-1}{\epsilon_1+2} \quad \text{when} \quad x_2 \to 0 \qquad \ldots (8)$$

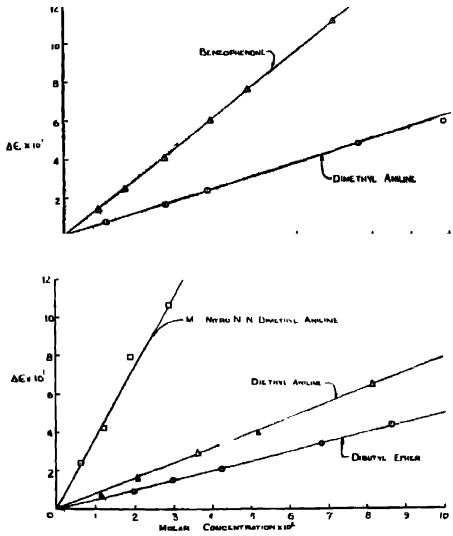
where a_2 is the radius of the cavity belonging to the solute molecule. For the calculation of a_2 we use

$$\left(\frac{3}{4\pi N_A}\right)^{\frac{1}{3}} \frac{n_2^2-1}{n_2^2+2} \qquad \ldots (9)$$

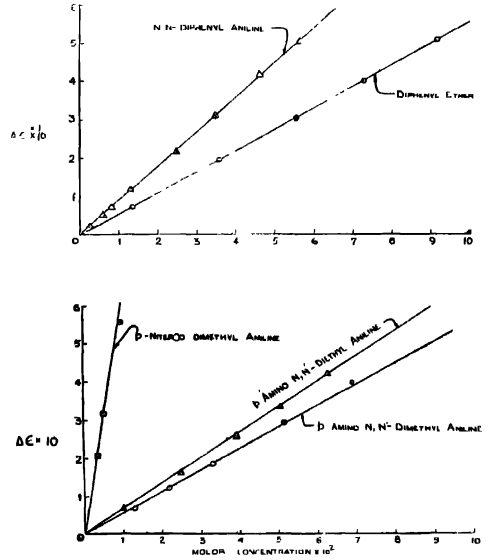
for simplification purpose.

The last term in the parenthesis in equation (6) being very small, is neglected and the value of μ are thus calculated.

Gilkerson & Srivastava equation (1960) aims at finding the dipole moment of a particular component in an n component system. This equation has been



Figures 1a, b. Plot of $\Delta\epsilon$ *vs* molar concentration of the solute.



Figures 2a, b. Plot of $\Delta\epsilon$ *vs* molar concentration of the solute.

reduced to a two component system (Srivastava & Gilkerson 1961) where polar-solute is dissolved in a non-polar solvent The dipole moment can be determined from the equation

$$\mu \quad \frac{12.1}{\epsilon_{\infty 2}+2}\left(\frac{2\epsilon+\epsilon_{\infty 2}}{2\epsilon+1}\right)^{\frac{1}{2}}\left(S-\frac{c_{\infty 2}}{C_2^0}\right)^{\frac{1}{2}} \qquad \ldots \quad (10)$$

where S is the slope of the plot of $\Delta\epsilon$ versus molar concentration of the solute. $\Delta\epsilon$ is given by

$$\Delta\epsilon = \epsilon - \epsilon_{\infty 1}\frac{C_1}{C_1^0} \qquad \ldots \quad (11)$$

where C_1^0 is the molar concentration of the pure solvent and C_2^0 corresponds to that of the pure solute.

Plots of dielectric constant ϵ, square of refractive index n_D^2, respectively, versus weight fraction of the solute, and that of dielectric constant, density respectively versus mole fraction have been made. These parameters sufficiently show a linear dependence with concentration in the dilute solution range. The

values of a_0, a , $(\partial c/\partial x_2)_0$, $(\partial d/\partial x_2)_0$ calculated from these plots are given in table 1 for all the molecules under study. Plots of $\Delta\varepsilon$ as defined by equation (11) versus molar concentration of the solute are made. It is observed that the linearity of these curves get extended over those plotted as a function of mole fraction. The values of S are calculated and are also given in the table.

Table 1

	a_0	a_D	$\left(\frac{\partial\varepsilon}{\partial x_2}\right)_0$	$\left(\frac{\partial d}{\partial x_2}\right)_0$	S	α_2 $\times 10^{23}$	f_2 $\times 10^{-21}$	$(1-f_2\alpha_2)$
N, N′-dimethylaniline	2.54	0.160	3.55	0 10	0.63	1.665	8.078	0.865
N, N′-diethylaniline	2 46	0.104	5.00	0 11	0 79	1.992	6.395	0.873
N, N′-diphenylaniline	0.68	0 422	2.00	0 61	0 91	2.723	3.655	0 900
m-Nitro-N, N′-dimethylaniline	17.40	0.210	36 7	0.48	3 64	1.751	9.059	0.841
p-Nitro-N, N′-dimethylaniline	29.5	0 45	62 5	0.56	6.11	1 751	9.059	0.841
p-Amino-N, N′-dimethylaniline	1 72	0.242	3.03	0 28	0 55	1 71	8 756	0.850
p-Amino-N, N′-diethylaniline	1 59	0.18	3.18	0.23	0.67	2.147	6.974	0.850
Diphenyl ether	1 13	0 218	2 71	0 35	0.56	2 092	7.300	0.848
Dibutyl ether	0.80	−0 357	1 25	−0.24	0.50	1.635	0 061	0.999
Benzophenone	5 90	0.281	13 21	0 45	1.615	2 185	6.96	0.842

Discussion

The values of the experimental dipole moments have been calculated by four methods and are given in table 2 along with the literature values.

A comparison of the moment values by the above mentioned four equations shows that in general, these values are higher in order by Scholte (1951) and Srivastava & Gilkerson equation, whereas there is a close agreement between the values obtained by Higasi (1952), Halverstadt & Kumler equations (1942). This situation is expected since both the former methods are based upon Onsager's equation (1936) whereas the latter methods are based upon Debye's equation (1912) Besides, it is also expected that the methods based upon Onsager's equation would correspond more closely to those observed in the vapour state since in their determination the solute-solute and solute-solvent interactions have been taken into consideration. On the contrary, the moment values calculated by Halverstadt & Kumler and Higasi's equations would be solvent dependent

Table 2

S. No	Substance	μ (Debye Units) Calculated by different methods				μ(McClellan 1963) (D)	
		Higasi	Halverstadt & Kumler	Scholte	Gilkerson & Srivastava		
1.	N.N′-dimethylaniline	1.59	1.51	1.63	1.75	1.61	
2.	N. N′-diethylaniline	1.76	1.71	1.98	1.98	1.81(B)	
3.	N, N′-diphenylaniline	0.13	0.38	1.37	1 95	0.65(B)	
4.	*m*-Nitro-N, N′-dimethylaniline	5.17	5.11	5.65	5.53	5.23	
5.	*p*-Nitro-N, N′-diethylaniline	6.73	6.74	7.54	7.16	6.20 to	6.96
6.	*p*-Amino-N, N′-dimethylaniline	1.33	1.37	1.60	1.46	1.43	
7.	*p*-Amino-N, N′-diethylaniline	1 42	1.43	1.63	1.56	—	
8.	Diphenyl ether	1.19	1.11	1.29	1.22	1.0,	1.36
9.	Dibutyl ether	1.13	1.06	1.49	1.35	(1.18),	1.26B
10.	Benzophenone	3.09	3.36	3.08	3.25	2.5 to	3 13

and also would not consider the solute-solute interactions. Here the directing field acting on a dipole is assumed to be equal to the internal field while directing field is always expected to be less than the internal field. Probably because of this very assumption the dipole moment values calculated by Halverstadt & Kumler and Higasi equations are less as compared to the other two equations.

However, the dipole moments calculated by different methods except for ***N, N′***-diphenylaniline in comparison with the literature values are reasonably good. In the case of diphenyl aniline the reaction field correction seems to be too much exaggerated. It will, therefore, be difficult to conclude which method will be better Nevertheless, if we consider the labour involved (i) in the calculations (ii) and additional measurement of the density data, then Higasi's method will get top priority particularly for the dipole moments in solutions.

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